Onverzadigde sulfocarbonzuren

Beute, Albert Engbertus

VI. SUMMARY OF RESULTS.

The purpose of this research was to prepare and to study the simplest unsaturated sulphocarboxylic acids.

By the interaction of α-bromoacrylic acid and sulphite in neutral solution *α-sulphoacrylic acid* was obtained:

$$CH_2 : CBr \,.\, CO_2K + K_2SO_3 = CH_2 : C(SO_3K) \,.\, CO_2K$$

The free acid crystallises with two molecules water (m.p. 87—88°). When dried in a desiccator, it only retains one molecule water. Among the salts, the acid aniline salt may serve for identification of the acid; it gives rhombic pyramidal crystals.

Addition of bisulfite to α-sulphoacrylic acid yields *α-β-disulphopropionic acid:*

$$CH_2 : C(SO_3K) . CO_2K + KHSO_3 = \\ = SO_3K . CH_2 . CH(SO_3K) . CO_2K$$

Other addition reactions were not observed.

Bromine substitutes hydrogen, with formation of *β-bromo-α-sulphoacrylic acid* and hydrobromic acid:

$$CH_2 : C(SO_3H) . CO_2H + Br_2 = CHBr : C(SO_3H) . CO_2H + HBr$$

It is not impossible, that the first phase of this reaction is an addition of bromine to the double bound, but in any case hydrobromic acid is split off directly.

Chlorine acts in the same way giving *β-chloro-α-sulphoacrylic acid.*

Addition of hydrochloric and hydrobromic acid or water to α-sulphoacrylic acid does not take place.

The oxidation of α-sulphoacrylic acid by permanganate was studied in neutral, alkaline and acid solution. In the presence of soda the oxidation gives the theoretical amount of oxalic acid and sulphate:

$$CH_2 : C(SO_3K) . CO_2K + 5O = CO_2H . CO_2H + CO_2 + K_2SO_4$$

The free α-sulphoacrylic acid, chlorinated with phosphorus pentachloride, gives a liquid dichloride (b.p. 111—115° at 25 mm). Exposed to the air, this chloride is converted into the cristalline monochloride (m.p. 115°):

$$CH_2 : C(SO_2Cl) . COCl + H_2O = CH_2 : C(SO_2Cl) . CO_2H$$

In order to obtain *β-sulphoacrylic acid,* β-chloroacrylic acid was prepared.

Addition of hydrochloric acid to propiolic acid (prepared from sodium carbide with compressed carbon dioxyde) gives two stereoisomeric *β-chloroacrylic acids,* melting at 63—64° and at 85.5—86°:

$$CH \vdots C . CO_2H + ClH = CHCl : CH . CO_2H$$

In chemical literature only the latter acid is known.

The potassium salt of the high melting acid is soluble in absolute

alcohol, whilst that of the low melting acid is not; thus the two isomerides may be separated.

By heating to 125°, the low melting acid is transformed into the isomeride.

The dissociation constants of both acids were measured by electrometric titration at 18°. The low melting isomeride was found to be the strongest acid, and therefore probably has the cis-structure [1]):

HCCl ‖ HCCO$_2$H	ClCH ‖ HCCO$_2$H
cis-β-chloroacrylic acid	trans-β-chloroacrylic acid
m.p. 63—64°. K = 4.77×10^{-4}	m.p. 85.5—86°. K = 2.22×10^{-3}

The reaction of high melting β-chloroacrylic acid with sulphite in neutral solution gives *α-sulphoacrylic acid* (characteristic acid aniline salt):

$$CHCl : CH . CO_2K + K_2SO_3 = CH_2 : C(SO_3K) . CO_2K + KCl.$$

This remarkable reaction may be due to an addition of bisulphite, followed by the loss of hydrochloric acid.

The reaction of low melting β-chloroacrylic acid with sulphite gives another sulphoacrylic acid; its barium and acid aniline salts differ totally from the salts of the α-isomeride.

The same acid is obtained by addition of bisulphite to propiolic acid. Thus it is probably β-sulphoacrylic acid:

$$CH \vdots C . CO_2K + KHSO_3 = SO_3K . CH : CH . CO_2K$$

This conclusion is in agreement with the different behaviour of the α- and β-acids to electrometric titration.

The free β-sulphoacrylic acid could not be obtained; by concentration in vacuo on sulphuric acid its aqueous solution is decomposed.

Addition of bisulphite gives α-β-disulphopropionic acid:

$$SO_3K . CH : CH . CO_2K + KHSO_3 = SO_3K . CH_2 . CH(SO_3K) . CO_2K$$

By the reaction of the two stereoisomeric α-bromo-crotonic acids

---

[1]) Recently Dr. A. E. v. Arkel has confirmed this conclusion by measuring the dipoles of the two isomerides.

with sulphite a *sulphocrotonic acid* is obtained, which may be identified by means of its acid aniline salt. As the same acid results from the reaction of sulphite with the two isomeric β-chlorocrotonic acids, its constitution is still uncertain.

An attempt to prepare β-sulphocrotonic acid by addition of one molecule bisulphite to tetrolic acid failed, as the unsaturated product could not be separated from α-β-disulphobutyric acid which was formed at the same time.

The free sulphocrotonic acid gives a monohydrate melting at 94—95°.

By addition of bisulphite α-β-disulphobutyric acid is formed:

$$\left.\begin{matrix} CH_3.C(SO_3K):CH.CO_2K \\ \text{or}\,CH_3.CH:C(SO_3K).CO_2K \end{matrix}\right\} + KHSO_3 = CH_3.CH(SO_3K).CH(SO_3K).CO_2K$$

The velocity of this reaction at 80° was measured. The reaction constant (K = 0.0633) was found to be much smaller than for the addition to crotonic acid (K = 0.187).

Sulphocrotonic acid reacts with bromine just as α-sulphoacrylic acid does; hydrogen bromide is split off and bromosulphocrotonic acid is obtained. The reaction with chlorine takes place in the same way. Addition of hydrobromic acid failed.

The two isomeric α-bromocrotonic acids (m.p. 106° and 92°), heated with absolute alcohol and sulphuric acid, produce the same *α-bromocrotonic ethyl ester*. It turned out, that the low melting α-bromoisocrotonic acid was isomerised into the high melting form by heating with dilute sulphuric acid.

However, the same ethyl ester is also formed by heating the silver salts of both α-bromocrotonic acids with ethyl iodide in absolute ether. The ester gives on saponification high melting α-bromocrotonic acid.

The action of α-β-dibromopropionic acid with sulphite yields *α-β-disulphopropionic acid:*

$$CH_2Br.CHBr.CO_2K + 2K_2SO_3 = SO_3K.CH_2.CH(SO_3K).CO_2K$$

The free acid gives a dihydrate melting at 91—93°. An attempt to separate the racemic acid into its enantiomorphs failed.

α-β-Disulphobutyric acid was not obtained by the reaction of α-β-dibromobutyric acid with sulphite, one of the bromine atomes was reduced with production of β-sulphobutyric acid (identified by means of its acid aniline salt):

$$CH_3 . CHBr . CHBr . CO_2K + 2K_2SO_3 + H_2O =$$
$$= CH_3 . CH(SO_3K) . CH_2 . CO_2K + KBr + HBr + K_2SO_4$$

However, the formation of α-β-disulphobutyric acid succeeded by addition of two molecules of bisulphite to tetrolic acid:

$$CH_3 . C \vdots C . CO_2K + 2KHSO_3 =$$
$$= CH_3 . CH(SO_3K) . CH(SO_3K) . CO_2K$$

α-β-Disulphobutyric acid forms a dihydrate melting at 83—84°.